

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 February 2003 (13.02.2003)

PCT

(10) International Publication Number
WO 03/011238 A2

(51) International Patent Classification⁷: **A61K 7/42**

(21) International Application Number: PCT/EP02/08010

(22) International Filing Date: 18 July 2002 (18.07.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01117748.2 31 July 2001 (31.07.2001) EP

(71) Applicant (*for all designated States except US*): **MERCK PATENT GMBH** [DE/DE]; Frankfurter Strasse 250, 64293 Darmstadt (DE).

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **HARIVEL, Anne-Cécile** [FR/FR]; 9, rue de la Marnière, F-94370 Sucy-en-Brie (FR).

(74) Common Representative: **MERCK PATENT GMBH**; Frankfurter Strasse 250, 64293 Darmstadt (DE).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SUNSCREEN COMPOSITION

(57) Abstract: The present invention relates to a foamable aqueous composition having UV protection properties comprising at least one hydrophobic organic sunscreen agent and at least one foam builder / stabiliser.



WO 03/011238 A2

- 1 -

Sunscreen composition

The present invention relates to sunscreen compositions.

5 A suntan of the skin to whatever degree is regarded in today's society as attractive and as an expression of vigour and sportiness. As well as this desired effect of the sun on the skin, a number of undesired secondary effects arise, such as sunburn or premature skin ageing and the development of wrinkles. In the meantime, a number of performance UV
10 filters have been developed which, applied to the skin in the form of creams, lotions or gels, can effectively delay the development of sunburn even when the incidence of solar rays is relatively high. The UV filter present in the pharmaceutical or cosmetic composition forms a film or a layer on the surface of the skin and does not penetrate into deeper skin
15 layers with other care substances present in the composition. Known UV filters or sun protection agents thus act only by absorbing certain regions of sunlight, meaning that this radiation cannot penetrate into deeper layers of the skin. As is known, the most hazardous part of solar radiation is formed by the ultraviolet rays having a wavelength of less than 400 nm. The lower
20 limit of the ultraviolet rays which reach the surface of the earth is limited by the absorption in the ozone layer to about 280 nm. The sun protection filters which are nowadays customary in cosmetics absorb in a wavelength range from 280 to 400 nm. This range includes UV-B rays having a wavelength between 280 and 320 nm, which play a decisive role in the
25 formation of a solar erythema, and also UV-A rays, having a wavelength between 320 and 400 nm, which tan the skin but also age it, favour the triggering of an erythematous reaction or can exacerbate this reaction in certain people or even trigger phototoxic or photoallergic and irritative reactions.

30

The object of care cosmetics is wherever possible to obtain the impression of a youthful skin. In principle, there are various ways of achieving this object. For example, existing skin damage, such as irregular pigmentation or the development of wrinkles can be smoothed out by covering powders
35 or creams. Another approach is to protect the skin against environmental influences which lead to permanent damage and thus ageing of the skin. The idea is therefore to intervene in a preventative manner and thus to delay the ageing process. One example of this is the UV filters already

- 2 -

mentioned which, as a result of absorption of certain wavelength regions, prevent or at least reduce skin damage. Depending on the position of their absorption maxima, UV absorbers for cosmetic and dermatological compositions are divided into UV-A and UV-B absorbers. UV-A absorbers
5 are usually also absorbing in the UV-B region and thus alternatively also being referred to as broad-band absorbers or broad-band filters.

Of decisive importance for the formulation is the solubility of the filter substances in the oil and water phases since it is necessary, particularly for
10 establishing a high protection factor, to incorporate filters into all phases of the formulation. The oil-soluble UV-B filters include isooctyl methoxycinnamate, isoamyl methoxycinnamate and methylbenzylidene-camphor. Examples of water-soluble UV filters are, in particular, the salts of 2-phenylbenzimidazole-5-sulfonic acid, the use of which as UV ray filter
15 has already been described in German Reichspatent No. 676 103.

In DE-A-199 55 375 a foamable sunscreen formulation being a oil-in-water-emulsion in a foam dispenser is described. The emulsion contains 2-50 % by weight of a oil phase and 50 to 98 % by weight of a water phase,
20 wherein the water phase contains a surfactant and the emulsion contains 1-40 % by weight of UV filters being divided between the oil and water phase in a manner that the water phase contains 0 to 10 % by weight of the filters and the oil phase contains 1 to 30 % by weight of the filters.

25 In the European patent application EP-A-0 193 932 a sunscreen composition for hair protection is disclosed. The composition comprises a mousse base or concentrate containing a sunscreen agent therein, said mousse base or concentrate comprising a cationic surfactant substantive to hair and a non-ionic film former which in combination with non-ionic
30 surfactant produces foam in the composition and upon application to hair forms a coating thereon. The composition is limited to water soluble or at least water miscible sunscreen agents.

There was therefore a need for a foamable sunscreen composition with
35 high sun protection factor (SPF) without giving an oily feeling when applied to the skin.

- 3 -

It has now surprisingly been found that this can be achieved with a aqueous composition comprising hydrophobic organic sunscreen agents and foam builder / stabilisers.

- 5 The present invention thus firstly provides a foamable aqueous composition having UV protection properties comprising at least one hydrophobic organic sunscreen agent and at least one foam builder / stabiliser.
- 10 Advantages of the compositions according to our invention are:
- High Sun protection factor (SPF).
 - Good photostability of the composition.
 - Hydrophobic UV filters are present in a purely aqueous formulation.
 - The oily impression which is often perceived as unpleasant upon
15 application of the preparation comprising hydrophobic UV filters is prevented.
 - Good applicability due to stable foam.

20 The foamable composition according to our invention is able to be foamed up with or without an propellant. According to our invention it is especially preferred if the foam is produced without the use of a organic propellant. Sprays using organic propellents may not be stored in direct sun or at higher temperatures; conditions that for example can often be found on the beach during summer. An advantage of preferred compositions according
25 to our invention is that the may be stored and used even under these conditions.

Therefore an embodiment of our invention is a kit of parts comprising a foam dispenser and a composition according to our invention. Suitable
30 foam dispensers are known to those skilled in the art. A preferred dispenser for this kit-of-parts is described in WO 00/78629.

The dispenser of WO 00/78629 is suitable for dispensing a liquid, in particular in the form of a foam, and comprises at least a liquid container
35 and a dispensing assembly which is coupled thereto at least in liquid-tight manner. A preferred dispensing assembly comprises a liquid pump with a liquid inlet and a liquid outlet and an actuating head. The actuating head comprises an outlet passage and a dispensing opening for dispensing the

- 4 -

liquid, while the actuating head furthermore comprises a closed, circumferential protective cap. The aerosol furthermore comprises a circumferential recess, into which the protective cap can move, which recess comprises a closed inner wall, an outer wall and a base. Preferably one or more outlet openings are present in the vicinity of the base of the recess, in which aerosol the shape of the recess is such that the inner wall, on the side which is remote from the base, is at a radial distance p from the protective cap, which distance p is greater than the usual clearance distance of the protective cap with respect to the inner wall. The disclosure of WO 00/78629 is enclosed herein by reference.

Preferred compositions are included in a foam dispenser, preferably in a foam dispenser that requires no organic propellant as described above.

As foam builders / stabilisers according to our invention in general all substances able to build or stabilise a foam may be used. Those substances in general are known to those skilled in the art. Preferred foam builders / stabilisers are those which are skin tolerant or even more preferably give a benefit to the skin.

The foam builders / stabilisers are usually present in an amount of about 0.01 to 20 % by weight, preferably in an amount of 0.1 to 5 % by weight and even more preferred in an amount of 0.1 to 3 % by weight.

In one embodiment of the invention preferred foam builders / stabilisers are cetyl phosphate, DEA cetyl phosphate, TEA myristate, TEA stearate, magnesium stearate, sodium stearate, potassium laurate, potassium ricinoleate, sodium cocoate, sodium tallowate, potassium castorate, sodium oleate and mixtures thereof.

In an preferred embodiment the foam stabilisers according to our invention are so called foam boosters. Foam boosters are substances which increase the surface viscosity of the liquid which surrounds the individual bubbles in a foam. These agents are commonly used in shaving soaps, shampoos, bubble baths, liquid soaps, mousses, or aerosol-dispensed foams. Also *Film Formers* or *Viscosity-Increasing Agents* maybe used as foam boosters. The listing below gives examples for foam boosters which can also be classified as surfactants (INCI names):

- 5 -

Acetamide MEA, Almondamide DEA, Almondamidopropylamine Oxide,
 Almondamidopropyl Betaine, Apricotamide DEA, Apricotamidopropyl
 Betaine, Avocadamide DEA, Avocadamidopropyl Betaine, Babassuamide
 DEA, Babassuamidopropylamine Oxide, Babassuamidopropyl Betaine,
 5 Behenamide DEA, Behenamide MEA, Behenamidopropyl Betaine,
 Behenamine Oxide, Behenyl Betaine, Canolamidopropyl Betaine,
 Capramide DEA, Carnitine, Cetearyl Alcohol, Cetyl Alcohol, Cetyl Betaine,
 Cocamide DEA, Cocamide MEA, Cocamide MIPA, Cocamidoethyl Betaine,
 Cocamidopropylamine Oxide, Cocamidopropyl Betaine, Cocamidopropyl
 10 Hydroxysultaine, Cocamine Oxide, Cocoamphodipropionic Acid,
 Cocobetainamido Amphopropionate, Coco-Betaine, Coco-Hydroxysultaine,
 Coco-Morpholine Oxide, Coconut Alcohol, Coco/Oleamidopropyl Betaine,
 Coco-Sultaine, Cocoyl Sarcosinamide DEA, DEA-Cocoamphodipropionate,
 DEA-Lauraminopropionate, Decyl Alcohol, Decylamine Oxide, Decyl
 15 Betaine, Diethanolaminooleamide DEA, Dihydroxyethyl C8-10
 Alkoxypropylamine Oxide, Dihydroxyethyl C9-11 Alkoxypropylamine Oxide,
 Dihydroxyethyl C12-15 Alkoxypropylamine Oxide, Dihydroxyethyl
 Cocamine Oxide, Dihydroxyethyl Lauramine Oxide, Dihydroxyethyl
 Stearamine Oxide, Dihydroxyethyl Tallowamine Oxide, Dimethicone Propyl
 20 PG-Betaine, Disodium Caproamphodiacetate, Disodium
 Caproamphodipropionate, Disodium Capryloamphodiacetate, Disodium
 Capryloamphodipropionate, Disodium Cetearyl Sulfosuccinate, Disodium
 Cocamido MIPA-Sulfosuccinate, Disodium Cocamido PEG-3
 Sulfosuccinate, Disodium Cocaminopropyl Iminodiacetate,
 25 Disodium Cocoamphocarboxyethylhydroxypropylsulfonate, Disodium
 Cocoamphodiacetate, Disodium Cocoamphodipropionate, Disodium C12-
 15 Pareth Sulfosuccinate, Disodium Deceth-5 Sulfosuccinate, Disodium
 Deceth-6 Sulfosuccinate, Disodium Hydrogenated Cottonseed Glyceride
 Sulfosuccinate, Disodium Isodecyl Sulfosuccinate, Disodium Isostearamido
 30 MEA-Sulfosuccinate, Disodium Isostearamido MIPA-Sulfosuccinate,
 Disodium Isostearamphodiacetate, Disodium
 Isostearamphodipropionate, Disodium Isostearyl Sulfosuccinate,
 Disodium Laneth-5 Sulfosuccinate, Disodium Lauramido MEA-
 Sulfosuccinate, Disodium Lauramido PEG-2 Sulfosuccinate, Disodium
 35 Laureth-5 Carboxyamphodiacetate, Disodium Laureth Sulfosuccinate,
 Disodium Laureth-6 Sulfosuccinate, Disodium Laureth-9 Sulfosuccinate,
 Disodium Laureth-12 Sulfosuccinate, Disodium Lauroamphodiacetate,
 Disodium Lauroamphodipropionate, Disodium Lauryl Sulfosuccinate,

- 6 -

Disodium Myristamido MEA-Sulfosuccinate, Disodium Nonoxynol-10
 Sulfosuccinate, Disodium Oleamido MEA-Sulfosuccinate, Disodium
 Oleamido MIPA-Sulfosuccinate, Disodium Oleamido PEG-2
 Sulfosuccinate, Disodium Oleoamphodipropionate, Disodium Oleth-3
 5 Sulfosuccinate, Disodium Oleyl Sulfosuccinate, Disodium Palmitamido
 PEG-2 Sulfosuccinate, Disodium Palmitoleamido PEG-2 Sulfosuccinate,
 Disodium PEG-4 Cocamido MIPA-Sulfosuccinate, Disodium PPG-2-
 Isodeceth-7 Carboxyamphodiacetate, Disodium Ricinoleamido MEA-
 Sulfosuccinate, Disodium Stearamido MEA-Sulfosuccinate, Disodium
 10 Stearoamphodiacetate, Disodium Stearyl Sulfosuccinamate, Disodium
 Stearyl Sulfosuccinate, Disodium Tallamido MEA-Sulfosuccinate, Disodium
 Tallowamido MEA-Sulfosuccinate, Disodium Tallowamphodiacetate,
 Disodium Tallow Sulfosuccinamate, Disodium Tridecylsulfosuccinate,
 Disodium Undecylenamido MEA-Sulfosuccinate, Disodium
 15 Undecylenamido PEG-2 Sulfosuccinate, Disodium Wheat Germamido
 MEA-Sulfosuccinate, Disodium Wheat Germamido PEG-2 Sulfosuccinate,
 Disodium Wheatgermamphodiacetate, Di-TEA-Oleamido PEG-2
 Sulfosuccinate, Ditridecyl Sodium Sulfosuccinate, Erucamidopropyl
 Hydroxysultaine, Hydrogenated Tallow Alcohol, Hydrogenated
 20 Tallowamide DEA, Hydrogenated Tallowamine Oxide, Hydrogenated
 Tallow Betaine, Hydroxyethyl Carboxymethyl Cocamidopropylamine,
 Hydroxyethyl Hydroxypropyl C12-15 Alkoxypropylamine Oxide,
 Hydroxystearamide MEA, Isostearamide DEA, Isostearamide MEA,
 Isostearamide MIPA, Isostearamidopropylamine Oxide,
 25 Isostearamidopropyl Betaine, Isostearamidopropyl Morpholine Oxide,
 Lactamide MEA, Lanolinamide DEA, Lauramide DEA, Lauramide MEA,
 Lauramide MIPA, Lauramide/Myristamide DEA, Lauramidopropylamine
 Oxide, Lauramidopropyl Betaine, Lauramine Oxide,
 Lauroamphodipropionic Acid, Lauryl Alcohol, Lauryl Betaine, Lauryl
 30 Hydroxysultaine, Lauryl Sultaine, Lecithinamide DEA, Linoleamide DEA,
 Linoleamide MEA, Linoleamide MIPA, Methyl Morpholine Oxide,
 Minkamide DEA, Minkamidopropylamine Oxide, Minkamidopropyl Betaine,
 Myristamide DEA, Myristamide MEA, Myristamide MIPA,
 Myristamidopropylamine Oxide, Myristamidopropyl Betaine, Myristamine
 35 Oxide, Myristaminopropionic Acid, Myristyl Alcohol, Myristyl Betaine,
 Myristyl/Cetyl Amine Oxide, Oleamide DEA, Oleamide MEA, Oleamide
 MIPA, Oleamidopropylamine Oxide, Oleamidopropyl Betaine,
 Oleamidopropyl Hydroxysultaine, Oleamine Oxide, Oleyl Betaine,

- 7 -

Olivamide DEA, Olivamidopropylamine Oxide, Olivamidopropyl Betaine,
 Palmamide DEA, Palmamide MEA, Palmamide MIPA, Palmamidopropyl
 Betaine, Palmitamide DEA, Palmitamide MEA, Palmitamidopropylamine
 Oxide, Palmitamidopropyl Betaine, Palmitamine Oxide, Palm Kernel
 5 Alcohol, Palm Kernelamide DEA, Palm Kernelamide MEA, Palm
 Kernelamide MIPA, Palm Kernelamidopropyl Betaine, Peanutamide MEA,
 Peanutamide MIPA, PEG-3 Cocamide, PEG-2 Hydrogenated Tallow
 Amine, PEG-3 Lauramide, PEG-3 Lauramide Oxide, PEG-2 Oleamide,
 PEG-3 Oleamide, PEG-2 Oleamine, PEG-2 Soyamine, PEG-2 Stearamine,
 10 Potassium Dihydroxyethyl Cocamine Oxide Phosphate, Ricinoleamide
 DEA, Ricinoleamide MEA, Ricinoleamide MIPA, Ricinoleamidopropyl
 Betaine, Sesamide DEA, Sesamidopropylamine Oxide, Sesamidopropyl
 Betaine, Sodium Caproamphoacetate, Sodium
 Caproamphohydroxypropylsulfonate, Sodium Caproamphopropionate,
 15 Sodium Capryloamphoacetate, Sodium
 Capryloamphohydroxypropylsulfonate, Sodium Capryloamphopropionate,
 Sodium Cocoamphoacetate, Sodium Cocoamphohydroxypropylsulfonate,
 Sodium Cocoamphopropionate, Sodium Cornamphopropionate, Sodium
 Isostearoamphoacetate, Sodium Isostearoamphopropionate, Sodium
 20 Lauramidopropyl Hydroxyphostaine, Sodium Lauraminopropionate, Sodium
 Lauriminodipropionate, Sodium Lauroamphoacetate, Sodium/MEA
 Laureth-2 Sulfosuccinate, Sodium Myristoamphoacetate, Sodium
 Oleoamphoacetate, Sodium Oleoamphohydroxypropylsulfonate, Sodium
 Oleoamphopropionate, Sodium Ricinoleoamphoacetate, Sodium
 25 Stearoamphoacetate, Sodium Stearoamphohydroxypropylsulfonate,
 Sodium Stearoamphopropionate, Sodium Tallamphopropionate, Sodium
 Tallowamphoacetate, Sodium Tallowate, Sodium
 Undecylenoamphoacetate, Sodium Undecylenoamphopropionate, Sodium
 Wheat Germamphoacetate, Soyamide DEA, Soyamidopropyl Betaine,
 30 Stearamide AMP, Stearamide DEA, Stearamide DEA-Distearate,
 Stearamide MEA, Stearamide MEA-Stearate, Stearamide MIPA,
 Stearamidopropylamine Oxide, Stearamidopropyl Betaine, Stearamine
 Oxide, Stearyl Alcohol, Stearyl Betaine, Tallamide DEA, Tallowamide DEA,
 Tallowamide MEA, Tallowamidopropylamine Oxide, Tallowamidopropyl
 35 Betaine, Tallowamidopropyl Hydroxysultaine, Tallowamine Oxide, Tallow
 Betaine, TEA-Lauraminopropionate, TEA-Myristaminopropionate,
 Trideceth-2 Carboxamide MEA, Trisodium Lauroampho PG-Acetate
 Phosphate Chloride, Undecylenamide DEA, Undecylenamide MEA,

- 8 -

Undecylenamidopropylamine Oxide, Undecylenamidopropyl Betaine, Wheat Germamide DEA, Wheat Germamidopropylamine Oxide, Wheat Germamidopropyl Betaine.

- 5 In one preferred embodiment of our invention the foaming composition of our foaming sunscreen formulation comprises
- (1) an alkylpolysaccharide surfactant having the formula $RO(R^1O)_tZ_x$ wherein Z is a moiety derived from a reducing saccharide containing from 5 to 6 carbon atoms, preferably a glucose, galactose, glucosyl, or
 10 galactosyl residue or mixtures thereof; R is a hydrophobic group selected from the group consisting of alkyl, alkyl phenyl, hydroxyalkyl phenyl or hydroxyalkyl groups or mixtures thereof in which said alkyl groups contain from about 8 to about 20 carbon atoms, most preferably from about 12 to about 14 carbon atoms; R¹ contains from 2 to 4
 15 carbon atoms, preferably ethylene, propylene and/or glyceryl, t is from 0 to about 30, preferably 0 to about 10, most preferably 0; wherein x is a number from about 1.5 to about 10, preferably 1.5 to 4, most preferably 1.6 to 2.7; and
- (2) an anionic cosurfactant which is a sulfate, sulfonate and/or carboxylate or mixtures thereof neutralized with one or more cationic moieties (M) to complete the formula, preferably the anionic cosurfactant has the
 20 formula $R^9(SO_3)_y(COO)_zM_q$; wherein R⁹ is an alkyl, alkylphenyl, hydroxyalkylphenyl or hydroxyalkyl, or mixtures thereof, said alkyl groups containing from about 6 to about 30 carbon atoms, preferably about 10 to about 18 carbon atoms; y is a number from 0 to about 4, z is a number from 0 to about 4, y + z is at least 1, and M is a cationic moiety with q being selected to complete the formula, wherein the
 25 ration of (2) to (1) is from about 1:10 to about 10:1 (i.e., 0.1 to 10.0). These surfactants mixtures are described in EP-A-070 074. It was
 30 found there that the cosurfactants interact with the alkylpolysaccharide surfactant to provide a stable foam.

In another even more preferred embodiment at least one foam builder / stabiliser is selected from foaming surfactants, preferably from
 35 alkylglycosides, anionic protein derivatives or fatty acid sulfonates.

An especially preferred foam builder / stabilisers are anionic protein derivatives, such as lipoaminoacids described in WO 98/09611,

- 9 -

WO 99/27902 and WO 99/45899. Most preferred under these anionic protein derivatives are sodium lauroyl oat amino acids, for example known as Proteol™ Oat (Tradename of Seppic).

- 5 In principle, all known UV filters are suitable for compositions according to our invention. Hydrophilic filters can be included in soluted form, while hydrophobic filters are included either in solid, dispersed or in encapsulated form. Particular preference is given to those UV filters whose physiological safety has already been demonstrated. There are many tried and tested
10 substances known from the specialist literature for both UVA and also UVB filters, e.g.

Benzylidenecamphor derivatives, such as

- 3-(4'-methylbenzylidene)-dl-camphor (e.g. Eusolex® 6300),
 - 15 - 3-benzylidenecamphor (e.g. Mexoryl® SD),
 - polymers of N-[(2 and 4)-[(2-oxoborn-3-ylidene)-methyl]benzyl]acrylamide (e.g. Mexoryl® SW),
 - N,N,N-trimethyl-4-(2-oxoborn-3-ylidenemethyl)anilinium methylsulfate (e.g. Mexoryl® SK) or
 - 20 - α -(2-oxoborn-3-ylidene)toluene-4-sulfonic acid (e.g. Mexoryl® SL),
- benzoyl- or dibenzoylmethanes, such as
- 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)propane-1,3-dione (e.g. Eusolex® 9020) or
 - 4-isopropylidibenzoylmethane (e.g. Eusolex® 8020),

25 benzophenones, such as

- 2-hydroxy-4-methoxybenzophenone (e.g. Eusolex® 4360) or
- 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid and its sodium salt (e.g. Uvinul® MS-40),

4,4,-diarylbutadienes as described in EP-A-0 916 335,

30 methoxycinnamic esters, such as

- octyl methoxycinnamate (e.g. Eusolex® 2292),
- isopentyl 4-methoxycinnamate, e.g. as a mixture of the isomers (e.g. Neo Heliopan® 1000),

salicylate derivatives, such as

- 35 - 2-ethylhexyl salicylate (e.g. Eusolex® OS),
- 4-isopropylbenzyl salicylate (e.g. Megasol®) or
- 3,3,5-trimethylcyclohexyl salicylate (e.g. Eusolex® HMS),
- 4-aminobenzoic acid and derivatives, such as

- 10 -

- 4-aminobenzoic acid,
- 2-ethylhexyl 4-(dimethylamino)benzoate (e.g. Eusolex[®] 6007),
- ethoxylated ethyl 4-aminobenzoate (e.g. Uvinul[®] P25),

5 and further substances, such as

- 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (e.g. Eusolex[®] OCR),
- 2-phenylbenzimidazole-5-sulfonic acid, and its potassium, sodium and triethanolamine salts (e.g. Eusolex[®] 232),
- 3,3'-(1,4-phenylenedimethylene)-bis(7,7-dimethyl-2-oxobicyclo[2.2.1]hept-1-ylmethanesulfonic acid and its salts (e.g. Mexoryl[®] SX) and
- 2,4,6-trianilino-(p-carbo-2'-ethylhexyl-1'-oxy)-1,3,5-triazine (e.g. Uvinul[®] T 150).

15 The compounds given in the list are only to be regarded as examples. It is of course also possible to use other UV filters.

Further suitable organic UV filters are, for example,

- 2-(2H-benzotriazol-2-yl)-4-methyl-6-(2-methyl-3-(1,3,3,3-tetramethyl-1-(trimethylsilyloxy)disiloxanyl)propyl)phenol (e.g. Silatrizole[®]),
- bis(2-ethylhexyl) 4,4'-[(6-[4-((1,1-dimethylethyl)aminocarbonyl)-phenylamino]-1,3,5-triazine-2,4-diyl)diimino]bisbenzoate (e.g. Uvasorb[®] HEB),
- α -(trimethylsilyl)- ω -[trimethylsilyloxy]poly[oxy(dimethyl [and about 6% methyl[2-[p-[2,2-bis(ethoxycarbonyl)vinyl]phenoxy]-1-methylenethyl] and about 1.5% methyl[3-[p-[2,2-bis(ethoxycarbonyl)-vinyl]phenoxy]propenyl] and 0.1 to 0.4% (methylhydrogen)silylene]] (n \approx 60) (CAS No. 207 574-74-1)
- 2,2'-methylenebis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol) (CAS No. 103 597-45-1)
- 2,2'-(1,4-phenylene)bis(1H-benzimidazol-4,6-disulfonic acid, mono-sodium salt) (CAS No. 180 898-37-7) and
- 2,4-bis[[4-(2-ethylhexyloxy)-2-hydroxyl]phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine (CAS No. 103 597-45-, 187 393-00-6).

35

These organic UV filters are usually incorporated into cosmetic formulations in an amount of from 0.5 to 20% by weight, preferably 1 - 15%.

- 11 -

Conceivable as inorganic UV filters are those from the group of titanium dioxides, such as, for example, coated titanium dioxide (e.g. Eusolex® T-2000, Eusolex® T-AQUA), zinc oxides (e.g. Sachtotec®), iron oxides and
5 also cerium oxides. These inorganic UV filters are generally incorporated into cosmetic formulations in an amount of from 0.5 to 20% by weight, preferably 2 - 10%.

Preferred compounds with UV-filtering properties are 3-(4'-methyl-
10 benzylidene)-dl-camphor, 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione, 4-isopropylidibenzoylmethane, 2-hydroxy-4-methoxybenzophenone, octyl methoxycinnamate, 3,3,5-trimethylcyclohexyl salicylate, 2-ethylhexyl 4-(dimethylamino)benzoate, 2-ethylhexyl 2-cyano-
15 3,3-diphenylacrylate, 2-phenylbenzimidazole-5-sulfonic acid, its potassium, sodium and triethanolamine salts and coated titanium dioxide.

By combining two or more compounds listed above it is possible to optimize the protective action against harmful effects of UV radiation. The combination of the above-mentioned UV filters in a formulation gives a
20 composition which combines light protection with particular mildness to the skin. All of the UV filters specified can also be used in encapsulated form. In particular according to our invention it is advantageous to use hydrophobic UV filters in encapsulated form.

25 In a preferred embodiment of our invention, the composition comprises at least one water-soluble organic sunscreen agent, preferably in an amount from 0.01 to 20 % by weight.

It is also preferred, if the composition comprises at least one inorganic
30 sunscreen agent, preferably at least one microparticulate inorganic sunscreen, most preferably selected from zinc or titanium dioxide.

It is therefore preferred according to the invention if one or more of the above-mentioned UV filters are present in encapsulated form. In this
35 connection, it is advantageous if the capsules are so small that they can not be observed with the naked eye. To achieve the above-mentioned effects, it is also necessary for the capsules to be sufficiently stable and not

- 12 -

to release the encapsulated active ingredient (UV filter) into the surroundings, or to release it only to a slight extent.

Suitable capsules can have walls made of inorganic or organic polymers. For example, US 6,242,099 B1 describes the preparation of suitable capsules with balls made of chitin, chitin derivatives or polyhydroxylated polyamines. Capsules which are to be used particularly preferably according to the invention have walls which can be obtained by a sol-gel process, as is described in the applications WO 00/09652, WO 00/72806 and WO 00/71084. Preference is given here in turn to capsules whose walls are made of silica gel (silica; undefined silicon oxide hydroxide). The preparation of corresponding capsules is known to the person skilled in the art, for example, from the cited patent applications, the contents of which also expressly belonging to the subject-matter of the present application.

Preferred capsules have a average particle size in the range from about 10 nm up to about 10000 nm, preferably up to 5000 nm and most preferred up to 2000 nm. The minimal particle size of those capsules depends on necessary size to prevent penetration of the skin. On the other side, the maximum particle size is limited by the application needs. The capsules shouldn't be discernible with blank eyes.

Here, the capsules are present in formulations according to the invention preferably in amounts which ensure that the encapsulated UV filters are present in the formulation in the amounts given above.

In a preferred embodiment of our invention at least one hydrophobic organic sunscreen is encapsulated, wherein the sunscreen is preferably encapsulated in capsules mainly consisting of organic polymeric materials or inorganic oxidic materials as described above.

In another preferred embodiment of our invention at least one hydrophobic organic sunscreen is immobilised by being attached to a surface, preferably to the surface of inorganic sunscreen particles. The sunscreen can be attached physically or chemically bonded. If the sunscreen is chemically bonded to the surface this may be directly or via an organic or inorganic spacer group.

- 13 -

The protecting action against oxidative stress or against the effect of free radicals can be further improved if the formulation comprises one or more antioxidants.

- 5 There are many tried and tested substances known from the specialist literature which can be used, e.g. amino acids (e.g. glycine, histidine, tyrosine, tryptophan) and derivatives thereof, imidazoles (e.g. urocanic acid) and derivatives thereof, peptides, such as D,L-carnosine, D-carnosine, L-carnosine and derivatives thereof (e.g. anserine), carotinoids, 10 carotenes (e.g. α -carotene, β -carotene, lycopene) and derivatives thereof, chlorogenic acid and derivatives thereof, lipoic acid and derivatives thereof (e.g. dihydrolipoic acid), aurothioglucose, propylthiouracil and other thiols (e.g. thioredoxin, glutathione, cysteine, cystine, cystamine and the glycosyl, N-acetyl, methyl, ethyl, propyl, amyl, butyl and lauryl, palmitoyl, oleyl, γ - 15 linoleyl, cholesteryl and glycerylestere thereof), and salts thereof, dilauryl thiodipropionate, distearyl thiodipropionate, thiodipropionic acid and derivatives thereof (esters, ethers, peptides, lipids, nucleotides, nucleosides and salts), and sulfoximine compounds (e.g. buthionine-sulfoximine, homocysteine-sulfoximine, buthionine-sulfone, penta-, hexa- 20 and heptathionine-sulfoximine) in very low tolerated doses (e.g. pmol to μ mol/kg), and also (metal) chelating agents, (e.g. α -hydroxy fatty acids, palmitic acid, phytic acid, lactoferrin), α -hydroxy acids (e.g. citric acid, lactic acid, malic acid), humic acid, bile acid, bile extracts, bilirubin, biliverdin, EDTA, EGTA and derivatives thereof, unsaturated fatty acids and 25 derivatives thereof, vitamin C and derivatives (e.g. ascorbyl palmitate, magnesium ascorbyl phosphate, ascorbyl acetate), tocopherols and derivatives (e.g. vitamin E acetate), vitamin A and derivatives (e.g. vitamin A palmitate), and coniferyl benzoate of benzoin resin, rutin and salts of the sulfuric ester of rutin and derivatives thereof, α -glycosyl rutin, ferulic acid, 30 furfurylidineglucitol, carosine, butylhydroxytoluene, butylhydroxyanisol, nordihydroguaretic acid, trihydroxybutyrophenone, quercetin, uric acid and derivatives thereof, mannose and derivatives thereof, zinc and derivatives thereof (e.g. ZnO, ZnSO₄), selenium and derivatives thereof (e.g. selenomethionine), stilbenes and derivatives thereof (e.g. stilbene oxide, 35 trans-stilbene oxide).

Mixtures of antioxidants are likewise suitable for use in the cosmetic formulations according to the invention. Known and commercial mixtures

- 14 -

are, for example, mixtures comprising, as active ingredients, lecithin, L-(+)-ascorbyl palmitate and citric acid (e.g. Oxydex[®] AP), natural tocopherols, L-(+)-ascorbyl palmitate, L-(+)-ascorbic acid and citric acid (e.g. Oxydex[®] K LIQUID), tocopherol extracts from natural sources, L-(+)-ascorbyl palmitate, L-(+)-ascorbic acid and citric acid (e.g. Oxydex[®] L LIQUID), DL- α -tocopherol, L-(+)-ascorbyl palmitate, citric acid and lecithin (e.g. Oxydex[®] LM) or butylhydroxytoluene (BHT), L-(+)-ascorbyl palmitate and citric acid (e.g. Oxydex[®] 2004).

10 The formulations according to the invention can comprise vitamins as further ingredients. Preferably, vitamins and vitamin derivatives chosen from vitamin A, vitamin A propionate, vitamin A palmitate, vitamin A acetate, retinol, vitamin B, thiamine chloride hydrochloride (vitamin B₁), riboflavin (vitamin B₂) nicotinamide, vitamin C (ascorbic acid), vitamin D, 15 ergocalciferol (vitamin D₂), vitamin E, DL- α -tocopherol, tocopherol E acetate, tocopherol hydrogensuccinate, vitamin K₁, esculin (vitamin P active ingredient), thiamine (vitamin B₁) nicotinic acid (niacin), pyridoxine, pyridoxal, pyridoxamine, (vitamin B₆), panthothenic acid, biotin, folic acid and cobalamine (vitamin B₁₂) are present in the cosmetic formulations according to the invention, particularly preferably vitamin A palmitate, 20 vitamin C, DL- α -tocopherol, tocopherol E acetate, nicotinic acid, panthothenic acid and biotin.

25 The composition of our invention can be a cosmetic formulation or a pharmaceutical formulation.

Any customary carriers, auxiliaries and optionally further active ingredients may be added to the formulation. Preferred auxiliaries originate from the group of preservatives, antioxidants, stabilizers, solubility promoters, 30 vitamins, colorants, odour improvers.

Further typically cosmetic application forms are also sunscreen, presun and aftersun compositions.

35 All compounds or components which can be used in the cosmetic or pharmaceutical formulations are either known and available commercially or can be synthesized by known processes.

- 15 -

The composition according to the invention is particularly suitable for protecting human skin against the harmful influences of the UV constituents in sunlight, in addition they also offer protection against ageing processes of the skin and against oxidative stress, i.e. against damage
5 caused by free radicals, as are produced, for example, by solar irradiation, heat or other influences.

Therefore the use of a composition according to our invention for the manufacture of a medicament suitable for the prophylaxis of damages of
10 the skin caused by sunray, especially for the prophylaxis of sunburn and sun-caused erythrema is another embodiment of our invention. A further embodiment is the cosmetic prophylaxis of damages of the skin caused by sunray, especially for the prophylaxis of sunburn and sun-caused erythrema.

15 The formulation may comprise adjuvants which are customarily used in this type of composition, such as, for example, thickeners, softeners, moisturizers, surface-active agents, emulsifiers, preservatives, perfumes, waxes, lanolin, propellants, dyes and/or pigments which colour the
20 composition itself or the skin, and other ingredients customarily used in cosmetics.

If a composition is formulated as an aerosol, the customary propellants, such as alkanes, fluoroalkanes and chlorofluoroalkanes may be used.
25

The cosmetic formulation can also be used to protect the hair against photochemical damage in order to prevent changes of colour shades, decoloration or damage of a mechanical nature. In this case, a suitable formulation is in the form of a shampoo or lotion for rinsing out, the
30 formulation in question being applied before or after shampooing, before or after colouring or bleaching or before or after permanent waving. It is also possible to choose a formulation in the form of a lotion or gel for styling or treating the hair, in the form of a lotion or gel for brushing or blow-waving, in the form of a hair lacquer, permanent waving composition, colorant or
35 bleach for the hair. The cosmetic formulation may comprise various adjuvants used in this type of composition, such as surface-active agents, thickeners, polymers, softeners, preservatives, foam stabilizers, electrolytes, organic solvents, silicone derivatives, antigrease agents, dyes

- 16 -

and/or pigments which colour the composition itself or the hair, or other ingredients customarily used for hair care.

5 To protect the skin and/or natural or sensitized hair against solar rays, the cosmetic composition is applied to the skin or the hair. Sensitized hair is understood here as meaning hair which has been subjected to a chemical treatment, such as a permanent waving treatment, a colouring process or bleaching process.

10 the compositions of our invention can be produced by mixing aqueous dispersions of encapsulated organic sunscreens and/or aqueous dispersions of inorganic sunscreen particles with other ingredients of the composition. This method for producing a sunscreen is another preferred embodiment of our invention.

15 The examples below illustrate the present invention in more detail without limiting the scope of the invention. The following trade names are used in the example formulations:

20 The silica capsules used in the examples can be obtained by a sol-gel process, as is described in the applications WO 00/09652, WO 00/72806 and WO 00/71084. The preparation of corresponding capsules is known to the person skilled in the art, for example, from the cited patent applications,
25 the contents of which also expressly belonging to the subject-matter of the present application.

- 17 -

Example 1: SUN PROTECTION SPRAY-Mousse

	supplier	% by weight
PHASE A		
Water, Titanium dioxide, Alumina, sodium metaphosphate, phenoxyethanol, sodium methyl paraben (Eusolex™ T aqua)	1	16.5
PHASE B		
Phenyl benzimidazole Sulfonic Acid (Eusolex™ 232)	1	3
Sodium hydroxyde	1	0.44
Water		10
PHASE C		
CI 77891 (Titanium dioxide), Mica, Silica (Timiron™ Splendid gold)	1	1
Sodium Lauroyl OAT Aminoacids (Proteol™ oat)	2	5
Dimethicone Copolyol Phosphate (Pecosil™ PS 100)	2	0.5
Disodium EDTA	1	0.1
Chlorphenesin	1	0.3
Glycerol	1	3
Water, demineralized		Qsp 100
PHASE D		
silica capsules OMC (Octylmethoxycinnamate: 42%)	1	23

5 **PROCEDURE :**

Phase A is dispersed in the Phase C. Then phase B and phase D are added and neutralized at pH=8.

Suppliers: 1 Merck
2 Seppic

10

- 18 -

Example 2: SUN PROTECTION SPRAY-Mousse

	supplier	% by weight
PHASE A		
Water, Titanium dioxide, Alumina, sodium metaphosphate, phenoxyethanol, sodium methyl paraben (Eusolex™ T aqua)	1	16
PHASE B		
Sodium Lauroyl OAT Aminoacids (Proteol™ oat)	2	5
Disodium EDTA	1	0.1
Chlorphenesin	1	0.3
Glycerol	1	3
Water, demineralized		Qsp 100
PHASE C		
silica capsules OMC (Octylmethoxycinnamate: 42%)	1	23

PROCEDURE :

- 5 Phase B is dispersed in the Phase A. Then phase C is added and neutralized at pH=5,5.

Suppliers: 1 Merck
2 Seppic

Example 3: SUN PROTECTION SPRAY-Mousse

	supplier	% by weight
PHASE A		
Water, Titanium dioxide, Alumina, sodium metaphosphate, phenoxyethanol, sodium methyl paraben (Eusolex™ T aqua)	1	16.5
PHASE B		
Phenyl benzimidazole Sulfonic Acid (Eusolex™ 232)	1	3
Sodium hydroxyde	1	0.44
Water		10
PHASE C		
Sodium Lauroyl OAT Aminoacids (Proteol™ oat)	2	5
Disodium EDTA	1	0.1
Chlorphenesin	1	0.3
Glycerol	1	3
Water, demineralized		Qsp 100
PHASE D		
silica capsules OMC (Octylmethoxycinnamate: 42%)	1	23

PROCEDURE :

- 5 Phase A is dispersed in the Phase C. Then phase B and phase D are added and neutralized at pH=8.
Suppliers: 1 Merck
 2 Seppic
- 10 The average SPC (3 measurements), measured for a layer of 2 mg/cm² on Transpore™ Tape (trademark of 3M) 20 min after application, is 22,4.

- 20 -

Example 4:

	Eusolex™ T aqua	16.5
	Eusolex™ 232	3
5	Eusolex™ 9020 in silica capsule	23
	Sodium hydroxyde	0.44
	Proteol™ oat	5
	Disodium EDTA	0.1
	Chlorphenesin1	0.3
10	Glycerol	3
	Water, demineralized	Qsp 100

Example 5:

15	Eusolex™ T aqua	16.5
	Eusolex™ 232	3
	Eusolex™ 6300 in silica capsule	20
	Sodium hydroxyde	0.44
20	Proteol™ oat	5
	Disodium EDTA	0.1
	Chlorphenesin1	0.3
	Glycerol	3
	Water, demineralized	Qsp 100
25		

Example 6:

	Eusolex™ T aqua	16.5
30	Eusolex™ 232	3
	Eusolex™ OCR in silica capsule	12
	Eusolex™ 9020 in silica capsule	12
	Sodium hydroxyde	0.44
	Proteol™ oat	5
35	Disodium EDTA	0.1
	Chlorphenesin1	0.3
	Glycerol	3
	Water, demineralized	Qsp 100

- 21 -

Example 7:

5	Eusolex™ T aqua	16.5
	Eusolex™ 232	3
	Eusolex™ 9020/OCR in silica capsule	12
	Eusolex™ 6300 in silica capsule	12
	Sodium hydroxyde	0.44
10	Proteol™ oat	5
	Disodium EDTA	0.1
	Chlorphenesin1	0.3
	Glycerol	3
	Water, demineralized	Qsp 100
15		

Example 8:

	Eusolex™ T-2000	12
20	Eusolex™ 232	3
	Eusolex™ 9020 in silica capsule	23
	Sodium hydroxyde	0.44
	Proteol™ oat	5
	Disodium EDTA	0.1
25	Chlorphenesin1	0.3
	Glycerol	3
	Water, demineralized	Qsp 100

- 22 -

Patent claims

1. Foamable aqueous composition having UV protection properties comprising at least one hydrophobic organic sunscreen agent and at least one foam builder / stabiliser.
5
2. Composition according to Claim 1, characterised in that the composition comprises at least one water-soluble organic sunscreen agent, preferably in an amount from 0.01 to 20 % by weight.
10
3. Composition according to at least one of the claims 1 or 2, characterised in that, the composition comprises at least one inorganic sunscreen agent, preferably at least one microparticulate inorganic sunscreen, most preferably selected from zink or titanium dioxide.
15
4. Composition according to at least one of the claims 1 to 3, characterised in that, at least one hydrophobic organic sunscreen is encapsulated, wherein the sunscreen is preferably encapsulated in capsules mainly consisting of organic polymeric materials and/or inorganic oxidic materials.
20
5. Composition according to at least one of the claims 1 to 4, characterised in that, at least one hydrophobic organic sunscreen is immobilised by being coupled to a surface, preferably to the surface of inorganic sunscreen particles.
25
6. Composition according to at least one of the claims 1 to 5, characterised in that the composition, comprises at least one compound from the group consisting of 3-(4'-methylbenzylidene)-dl-camphor, 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)propane-1,3-dione, 4-isopropylidibenzoylmethane, 2-hydroxy-4-methoxybenzophenone, octyl methoxycinnamate, 3,3,5-trimethyl-cyclohexyl salicylate, 2-ethylhexyl 4-(dimethylamino)benzoate, 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, its potassium, sodium and triethanolamine salts and coated titanium dioxide.
30
35

- 23 -

- 5 7. Composition according to at least one of the claims 1 to 6, characterised in that the at least one foam builder / stabiliser is selected from foaming surfactants, preferably from alkylglycosides, anionic protein derivatives, fatty acid sulfonates ... and most preferred the at least one foam builder / stabiliser is a anionic protein derivative.
- 10 8. Composition according to at least one of the claims 1 to 7, characterised in that the composition is a cosmetic formulation.
- 15 9. Composition according to at least one of the claims 1 to 8, characterised in that the composition is a pharmaceutical formulation.
- 20 10. Composition according to at least one of the claims 1 to 9, characterised in that the composition is included in a foam dispenser, preferably in a foam dispenser that requires no propellant gas.
- 25 11. Use of a composition according to at least one of the claims 1 to 10 for the manufacture of a medicament suitable for the prophylaxis of damages of the skin caused by sunray, especially for the prophylaxis of sunburn and sun-caused erythrema.
- 30 12. Use of a composition according to at least one of the claims 1 to 10 for the cosmetic prophylaxis of damages of the skin caused by sunray, especially for the prophylaxis of sunburn and sun-caused erythrema.
- 35 13. Kit of parts comprising a foam dispenser and a composition according to at least one of the claims 1 to 10.
14. Method for producing a sunscreen composition by mixing aqueous dispersions of encapsulated sunscreens and/or aqueous dispersions of inorganic sunscreen particles with other ingredients of the composition.